

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number
WO 01/92366 A1

(51) International Patent Classification⁷: **C08G 18/80**,
18/66

(21) International Application Number: PCT/US00/14722

(22) International Filing Date: 25 May 2000 (25.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **BAT-
TELLE MEMORIAL INSTITUTE** [US/US]; 505 King
Avenue, Columbus, OH 43210-2693 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BENECKE, Her-
man, P.** [US/US]; 920 Lansmere Lane, Columbus, OH
43220 (US). **MARKLE, Richard, A.** [US/US]; 1083 Nor-
way Drive, Columbus, OH 43221 (US).

(74) Agents: **GOLDSTEIN, Steven, J.** et al.; Frost & Jacobs
LLP, 2500 PNC Center, 201 East Fifth Street, Cincinnati,
OH 45202 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,
TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: REVERSIBLE CROSSLINKED POLYMERS, BENZYL CROSSLINKERS AND METHOD

(57) Abstract: A polymer having a crosslinked structure made from a polyol and an isocyanate where the crosslinks are a urethane bond made from the reaction of a benzylic hydroxyl group and an isocyanate group.

WO 01/92366 A1

REVERSIBLE CROSSLINKED POLYMERS, BENZYL CROSSLINKERS AND METHOD

FIELD OF THE INVENTION

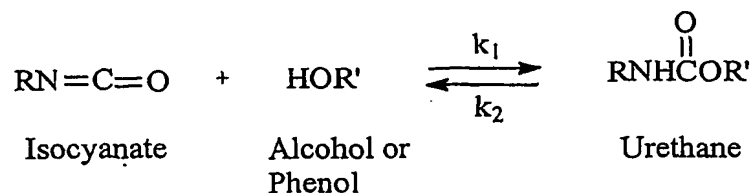
The invention involves crosslinked polyurethanes and other polymers not conventionally known as polyurethanes, with added urethane crosslinks where the , crosslinkers are based on compounds having one or more benzylic hydroxyl groups, and methods of making the polymers and crosslinkers. The polymers are useful to make fibers, sheets, moldings, coatings and other articles typically produced from polymers.

BACKGROUND OF THE INVENTION

Organic polyisocyanates have been used with compounds having active hydrogen groups, such as hydroxyl groups, to produce a wide variety of useful materials such as coatings, hot-melt adhesives, moldings. The materials have been used in injection molding applications and in composite or laminate fabrications. Typical of the art is the patent to Markle et al, US 5,097,010.

Urethane bonds are used ubiquitously in polymer chemistry to produce a wide variety of useful compositions.

The urethane bond is conveniently obtained by the addition reaction of an isocyanate group (either an aliphatic or an aromatic isocyanate) and an aliphatic alcohol or an aromatic (also known as aryl) hydroxyl group (a phenolic group). This reaction is reversible at sufficiently high temperatures as indicated by showing the following reaction as an equilibrium process.



In this equation, R is alkyl or aryl and R' independently is alkyl or aryl. The equilibrium constant K is defined as k_1/k_2 where k_1 is the rate constant of the forward, or urethane forming reaction, where k_2 is the rate constant of the reverse reaction involving reformation of RNCO and R'OH. These rate constants each vary as a function of the temperature, with k_1 and k_2 both increasing as the temperature increases. However, k_1 will dominate (i.e., $k_1 \gg k_2$) over some temperature range between ambient temperature and some intermediate higher temperature since the forward reaction typically has a lower activation energy than the reverse reaction. As a result of these activation energy differences, k_2 will increase more rapidly than k_1 as the temperature is increased. Thus, at some higher temperature, k_2 may equal k_1 (where the equilibrium constant $K = 1$) and may in certain cases become appreciably greater than k_1 at still higher temperatures. Hence, the equilibrium constant will range from quite high values at ambient temperature but can become relatively smaller at sufficiently high temperatures so that significant and useful concentrations of isocyanate groups will be present.

The forward, or urethane forming reaction, can be affected by simply heating an equimolar mixture of isocyanate and hydroxyl groups to the temperature at which k_1 is large enough that urethane formation occurs in an acceptable, or practical, period of time (from a few minutes to several hours). Catalysts, such as tertiary amines or certain organotin compounds, can speed both the forward and reverse processes but that are not necessary to bring about the urethane forming reaction or the establishment of equilibrium. If both compound types are difunctional, that is, if they are diisocyanates and dialcohols or diphenols, the forward reaction will produce polymeric products (polyurethanes) of very high molecular weights. The achievable molecular weight of fully reacted (i.e., of essentially non-reversed) pairs will be limited

by the presence and concentration of monofunctional isocyanates or monofunctional alcohols; by the isocyanate concentration and the dialcohol or the diphenol concentrations not being equal to each other; or, by the intervention of adventitious impurities which deplete the amount of either NCO or OH by side reactions. However, as the temperature of the polyurethane is further increased and k_2 increases faster in comparison to the increase in k_1 , significant and measurable reverse reaction to isocyanate and either alcohol or phenol will occur. The approximate reversal temperatures of urethanes derived from representative combinations of aliphatic or aryl isocyanates and alkyl or aryl hydroxyl groups (as defined earlier) have been previously reported by Z.W. Wicks, Jr., "Blocked Isocyanates" Progress in Organic Coatings, 3, pp. 73-99 (1975) as shown in Table 1 below:

Table 1

Isocyanate Type	Alcohol Type	Approximate Urethane Onset of Reversal Temperature (°C)
Aryl (e.g. MD1)	Aryl (e.g. Phenol)	120
Alkyl (e.g. HD1)	Aryl (e.g. Phenol)	180
Aryl (e.g. MD1)	Alkyl (e.g. n Butanol)	200
Alkyl (e.g. HD1)	Alkyl (e.g. n Butanol)	250

These temperatures are or approximate values which represent the onset of reversal or a temperature where the practical effect of reversal, such as the onset of distillation or evaporation of phenol or butanol from a heated mixture, or where infrared spectroscopy of heated samples can record the onset of isocyanate and alcohol or phenol formation from a previously unreversed urethane compound.

In the work described herein, it was sought to identify combinations of particular diisocyanates or polyisocyanates and dialcohols or diphenols, or polyalcohols or polyphenols, which would possess reversibility of practical utility (described further below) in terms of some relatively high temperature at which onset of reversibility would occur. This would allow the preparation

of polymers with both backbone urethane bonds (i.e. urethane bonds as part of the structure of the long molecular strands constituting a polymer chain), and crosslinking urethane bonds (i.e. urethane bonds connecting two of the long molecular strands constituting a polymer chain with bridging bonds, which result in dramatic increases in average molecular weight, such as for example a doubling thereof) which might be expected to have practical utility up to, or very close to, the temperature of onset of significant reversibility as described above. If sufficient reversible bonds, including latent crosslinks, are incorporated into such a reversible bond-containing polymer structure, polymers may be formed at some elevated temperature, by first heating the mixture of reactive components to some temperature above the practical onset of reversibility temperature such that a mixture of molten, or dissolved, partially assembled, urethane bond-containing, polymer fragments is established. As this mixture is cooled below this reversibility onset temperature, the polymer forming isocyanates and hydroxyl functional groups will fully form (or reform) urethane bonds providing a high molecular weight, crosslinked, polymer structure. Depending on the degree of crosslinking, the polymer product will be insoluble in a known solvent for the uncrosslinked polymer. But will swell in such a solvent to various degrees ranging from nil at high levels of crosslinking to moderate to high swell (e.g. 10 or more times increase in volume) at low levels. Low to high crosslinking levels, or crosslinking density, may range from about one crosslink per 100 to 200 or more polymer backbone repeat units, to one crosslink per 3 to 5 backbone repeat units. The higher levels of crosslinking are expected to show great utility in terms of mechanical (such as tensile or flexural) strength, rigidity (i.e. very high modulus values) scratch or abrasion resistance, resistance to organic solvents or water or various pH aqueous solutions, and other important properties, when used in such practical applications as molded parts, composite structures (e.g. glass fiber or fabric, carbon fiber or fabric, various particulate, and the like, filled structures), coatings on various substrates such as metals, glass reinforced moldings or composites, ceramics, silicon wafers or electronic components, and so on, very strong, including

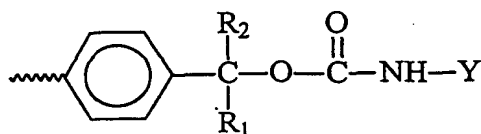
structural strength, adhesives for use to bond substrates such as described for coatings, and in other useful applications. These useful properties are expected to be obtained from subambient temperatures up to temperatures of 150°C or higher, or in some cases up to about 180°C or higher.

5 The need exists for new materials having both improved processing and end use characteristics. The present invention seeks to address those needs.

BRIEF DESCRIPTION OF THE INVENTION

10 Broadly the invention discloses a polymer having a crosslinked structure wherein the crosslinked structure comprises one or more urethane bonds made by the reaction of a benzylic hydroxyl group and an isocyanate group. A further embodiment provides for one or more urethane bonds made by the reaction of a benzylic hydroxyl group and an isocyanate group that are
15 also present in the polymer backbone of individual polymer chains. Typically the one or more of the urethane bonds begins to dissociate at a temperature above about 150°C

A further embodiment of the invention includes a polymer described above, wherein the crosslinked structure is:



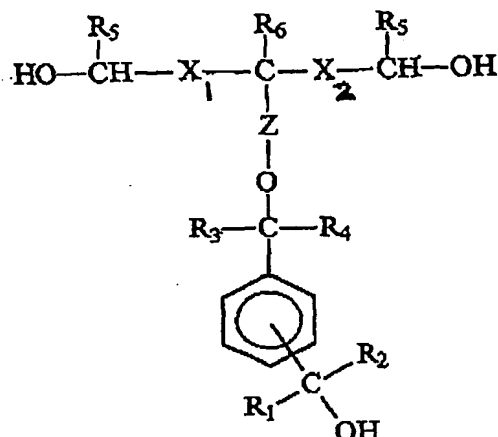
and wherein R₁ is H, and R₂ represents a group selected from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen groups;
25 and Y represents a group selected from an isocyanate residue. Typically the isocyanate residue is selected from the group consisting of monoisocyanate, diisocyanate, and triisocyanate residues. The isocyanate residue may also be selected from the group consisting of aromatic monoisocyanate, aromatic,

diisocyanate, aromatic triisocyanate, benzylic monoisocyanate, benzylic diisocyanate, benzylic triisocyanate, aliphatic monoisocyanate, aliphatic diisocyanate, and aliphatic triisocyanate residues. In some typical embodiments the polymer is a polyurethane and 0.01 to 99% of the urethane bonds in the polyurethane are obtained by reaction between a benzylic hydroxyl group and an isocyanate group. In other typical embodiments the polymer is a polyurethane and 0.1 to 50% of the urethane bonds in the polyurethane are obtained by reaction between a benzylic hydroxyl group and an isocyanate group

A yet further embodiment of the invention includes a polymer having a crosslinked structure including a polyol with a high molecular weight; a polyisocyanate; a polyol with a low molecular weight; and trifunctional crosslinking compound selected from the group: (1) a compound having one benzylic hydroxyl group and two aliphatic hydroxyl groups; (2) a compound having two benzylic hydroxyl groups and one aliphatic hydroxyl group; (3) a compound having three benzylic hydroxyl groups; and wherein 0.01 to 99 mol % of bonds in the crosslinked structure comprise urethane bonds obtained by the reaction between a benzylic hydroxyl group and an isocyanate group.

A yet further embodiment includes a polymer having a crosslinked structure of a polyol; a polyisocyanate; a trifunctional crosslinking compound selected from the group: (1) a compound having one benzylic hydroxyl group and two aliphatic hydroxyl groups; (2) a compound having two benzylic hydroxyl groups and one aliphatic hydroxyl group; (3) a compound having three benzylic hydroxyl groups; and wherein 0.01 to 99 mol % of bonds in the crosslinked structure comprise urethane bonds obtained by the reaction between a benzylic hydroxyl group and an isocyanate group.

An additional embodiment includes a compound such as:



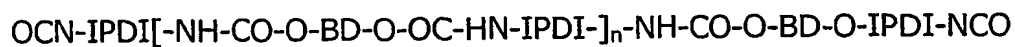
wherein R_1 and R_2 are identical or different and represent a group selected from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen groups; wherein R_3 and R_4 are identical or different and represent a group selected from -H, and hydrocarbon groups containing up to ten carbon atoms;
 5 R_5 represents hydrogen, methyl, ethyl, or propyl; R_6 represents hydrogen, methyl, or ethyl; X_1 (left arm), X_2 (right arm) and Z may be the same or different and represent none (no additional segment present), methylene, ethylene, or p-phenylene; the benzylic hydroxyl moiety may be positioned the para, meta or ortho position. In a preferred embodiment the compound is
 10 2-([(4-hydroxymethyl)benzyl]oxy)-1,3-propanediol. Another embodiment includes the use of this compound to crosslink neighboring polymer chains.

An additional embodiment includes a compound of a poly-benzylic hydroxyl group capped polymer or oligomer obtained by reacting compounds containing one primary aliphatic hydroxyl group and one or more benzylic
 15 hydroxyl groups with low molecular weight polyisocyanates in a molar ratio of one primary aliphatic hydroxyl group per isocyanate group in the polyisocyanate.

Other embodiments include crosslinker compositions consisting of bis-isocyanate capped low molecular weight polyols, which structures result from
 20 the reaction of 2-20 moles of diisocyanates as represented by OCN-R-NCOO where R is aliphatic, cycloaliphatic, bisbenzylic, or aromatic, with 1 mole of low molecular weight diols which include aliphatic diols with from 2 to 18 carbon atoms, cycloaliphatic diols with from 5 to 12 carbon atoms and bis-

(beta-hydroxyethyl) or bis-(beta-hydroxyethoxy) substituted aromatic rings, including benzene, naphthalene, pyridine or pyrazine rings. This embodiment likewise includes the use of the crosslinker compositions to crosslink polymers containing 1 or more pendant benzylic hydroxyl groups on the backbone of the polymer.

Another embodiment includes a crosslinker composition consisting of isophorone diisocyanate or TMXPI diisocyanate capped 1,4-butane diol such that a short oligomeric product described by the formula or expression



where $n = 0, 1, 2, 3, 4, 5$, etc. but is predominately 0.

is provided, and in which IPDI may be replaced with TMXDI, and is useful as a crosslinker of polymers containing pendant benzylic-hydroxyl groups.

BRIEF DESCRIPTION OF THE DRAWINGS

The Figure illustrates a method for producing Compound 1 including chemical structures associated with starting materials, intermediates, byproducts, and final product.

DETAILED DESCRIPTION OF THE INVENTION AND BEST MODE

This invention meets the needs for new polymers by providing thermally reversible polymer compositions having reversible polyurethane linkages in crosslinks between neighboring chains. The number of crosslinks can be controlled so as to obtain polymers with desired properties. The polyurethane crosslinks are based on bonds from benzylic hydroxyl groups and isocyanate groups. New compounds having such groups are also disclosed herein so as to achieve the desired reversible characteristics.

Broadly the invention discloses new materials and methods for preparing and crosslinking polymers to form polyurethanes, and other polymers not conventionally known as polyurethanes that consist of polymers

with added urethane crosslinks, having enhanced properties. One broad embodiment of the invention discloses new crosslinkers useful for obtaining polymers with enhanced properties. Another broad embodiment of the invention discloses new polymers obtained with the new crosslinkers. Other broad embodiments of the invention include methods and processes for preparing the polymers and crosslinkers. Yet another embodiment discloses selective preparation of new oligomeric chain extenders and crosslinkers derived from a simple compound type containing only one benzylic hydroxyl group and one primary aliphatic hydroxyl group.

Preliminary Tests

In order to identify more specific types of isocyanate groups and alcohol or phenol groups which might be expected to provide reversibility temperatures to meet these criteria and needs, some preliminary work was carried out using model compounds. These were based on the benzylic hydroxyl group (an aralkyl hydroxyl group intermediate, between a normal aliphatic hydroxyl group and the pure aromatic hydroxyl group of a phenol) as represented by p-hydroxymethylbenzoic acid (HMB), the phenol group of p-hydroxybenzoic acid (PHBA) and the cycloaliphatic isocyanate groups of isophoronediiisocyanate (IPDI) and the araalkyl isocyanate groups of TMXDI (1,3-bis(1-isocyanato-1-methyl-ethyl) benzene). The isocyanate groups of IPDI and TMXDI are both expected to result in an onset reversibility temperature intermediate between an aromatic diisocyanate (such as MDI) and an aliphatic diisocyanate such as HDI, with any given hydroxyl group. Likewise, the benzylic hydroxyl group is expected to result in an onset reversibility temperature intermediate between a normal aliphatic alcohol such as n-butanol (or a n-aliphatic diol such as 1,4-butanediol) and a phenol hydroxyl group. Hence, the following three pairings to be used in infrared spectroscopy determinations of approximate reversibility onset temperature were studied:

1. Phenolic-OH (from excess PHBA reacted with BD, Example A1) and IPDI-NCO (from an IPDI-BD-IPDI product with terminal NCO groups) Example C1.
2. Benzylic-OH (from HMB reacted with 1-octadecanol or C18 alcohol) to give a nonvolatile, ester-linked hydroxylmethyl benzoate, Example A2 and the same IPDI-NCO as above, Example C1.
3. Benzylic-OH (Example A2) and TMXDI-NCO (from a TMXDI-BD-TMXDI product with terminal NCO groups, Example C2).

The preparation of the PHBA-BD and HMB-C18 alcohol products is described in Example A1 and Example A2. The preparation of the three sets of products listed above for infrared spectroscopic (IR) interrogation as a function of temperature, to determine the approximate reversibility onset temperature and the quasi-midpoint of reversibility temperature is described in Example A3.

For the IR analysis, the samples were scanned in transmission mode using a Digilab FTS-60A, FT-spectrometer at 4 cm^{-1} resolution. The sample, as prepared as described in Example A3, and placed in the sample holder, between two 2 mm thick KBr salt plates. The IR samples were estimated to be about 0.1 mm thick. The sample holder was custom made by Harrick and is equipped with a resistance heater and coolant circulation connections for cooling the cell. The cell was heated and cooled with Therminol 59, a heat transfer fluid. For the IR measurements, the sample was heated from room temperature to 230°C ($\sim 5^{\circ}\text{C}/\text{min}$) and then cooled to room temperature ($\sim 82^{\circ}\text{C}/\text{min}$). After data collection, the peak intensities of the isocyanate ($\sim 2257\text{ cm}^{-1}$) and aromatic substitution absorption bands ($700\text{--}760\text{ cm}^{-1}$) were measured and this ratio was then shown plotted versus the temperatures at which the isocyanate ratios occurred. The isocyanate/aromatic substitution absorption ratio was used to compensate for the potential change in sample thickness during the temperature increases and decreases.

The first heatup of samples from room temperature to 230°C showed isocyanate absorptions already present even at room temperature, before heatup was started. This was presumed to be due to incomplete reaction of the NCO-OH pairs prepared in Example A3. However after this first heating and cooling cycle, the room temperature isocyanate absorption at 2259 cm⁻¹ was gone, indicating that the reaction was completed.

Based on the models in these tests, it was expected to see reversible temperatures ranging from about 160 to 210°C. As expected, the IR analysis of the system Pair 1, Pair 2 and Pair 3 pairs indicated midpoint reversion temperatures of about 175°C, 195°C, and 197°C respectively (Table 2). Most importantly in these tests, both Pair 2 and Pair 3 have a midpoint reversion temperature in the target range of 190-200°C and both are higher than the reversion temperature of Pair 1. This means the benzylic hydroxyl formed a more stable urethane bond than the phenol groups as expected. In fact, based on the pre-defined process temperature range (190-200°C), both Pair 2 and Pair 3 have acceptable reversible temperatures for fiber spinning at 195°C. Hence, Compound 1, having three functional groups, a reversible benzylic hydroxyl group available for crosslinking and two primary aliphatic groups available for incorporation into the polymer backbone, was synthesized for incorporation in a polymer via urethane linkages, in particular a thermoplastic elastic polyurethane. It was expected that Compound 1 would polymerize with a diisocyanate like MDI by forming very stable urethane bonds via the two primary aliphatic hydroxyl groups, but with a pendant unreacted benzylic hydroxyl group.

Table 2. Approximate Onset and Quasi-Midpoint Reversibility

Temperature for the Urethane Types

Pairs	Isocyanate Oligomers	Alcohol or Phenol Oligomers	Urethane Types	Approximate Onset Reversibility Temp. C	Quasi-Midpoint Reversibility Temp. C
1	IPDI-BD	PHBA-BD (phenolic)	Secondary Cycloaliphatic Isocyanate – Phenolic	105	175
2	IPDI-BD	HMB-C18 (benzylic)	Secondary Cycloaliphatic Isocyanate – Benzylic Alcohol	150	195
3	TMXDI-BD	HMB-C18 (benzylic)	Aromatic Substituted Tertiary Isocyanate – Benzylic Alcohol	140	197

5

EXAMPLE A1 – PHBA-BD Oligomers

p-Hydroxy benzoic acid (PHBA, Aldrich H2,005-9, as received) (60g, 0.435 mole) and butanediol (BD, Aldrich 24,055-9, vacuum distilled) (19.5g, 0.217 mole) were added to a round bottom flask fitted with a refluxing condenser. The contents were heated to 260°C for two hours. The water produced from the reaction was removed with a constant flow of nitrogen. To remove phenol which was formed as a byproduct, the oligoester was extracted with methanol and the methanol insoluble PHBA-BD portion was isolated. Then, the methanol soluble PHBA-BD was precipitated twice in water. The methanol soluble PHBA-BD was redissolved in acetone and reprecipitated in water. Both the methanol soluble and insoluble materials were analyzed by H-NMR which did not detect the presence of phenol. The methanol insoluble phenolic product was used in the model reversibility studies.

20

EXAMPLE A2 – HMB-C18 Oligomers

4-Hydroxymethyl benzoic acid (HMB) (6g, 0.03mole) and n-octadecanol (C18)(10.67g, 0.039mole) were added to a round bottom flask fitted with a refluxing condenser. The contents were heated to 260°C for two hours. The water produced from the reaction was removed with a constant flow of nitrogen. After the reaction, the HMB-C18 crude product was dissolved in 10 ml acetone and reprecipitated from 100 ml of methanol to remove the unreacted HMB. The H-NMR of this product indicated 20 mole percent of unreacted n-octadecanol. The unreacted n-octadecanol was removed by dissolving the HMB-C18 in methylene chloride and precipitating from hexane, which is a solvent for 1-octadecanol, before it was used for the reactive blending study.

EXAMPLE A3 – IPDI-BD and PHBA-BD

The isocyanate containing oligomers and hydroxyl containing oligomers were weighted into dry test tubes. They were combined in weight ratios such that equal molar amounts of NCD and OH groups were present. The mixtures were then heated to 160°C under a blanket of Argon with the test tube immersed in a heated Wood's metal bath. The reaction mixtures were maintained at 160°C for about 20 minutes with intermittent stirring under an argon gas purge. After the reaction, thin films were prepared from the oligomer reactive blended materials by pressing at about 180-190°C between 10 mil sheets of Teflon on a surface temperature controlled hot plate. The films were then analyzed by FT-IR by pressing between the IR plates. Two showed incomplete reaction after blending. That is some unreacted isocyanate was still present in the IR spectrum at room temperature. However, urethane formation was driven to completion by heating rapidly from room temperature to 230°C, and then cooling back to ambient temperature, as evidenced in the infrared spectroscopy (IR) performed in a scanning cell having heat-up and cool-down capability. IR spectra at the end of cycle one then showed that no free isocyanate remained. Hence, the IR

spectra for cycle 2 were taken as representative of the onset of the urethane reversing reaction and were used for the analysis.

In a general embodiment, the invention discloses new polymers that contain urethane based crosslinks that start to reversibly dissociate at temperatures at about 150°C so as to obtain appropriate melt viscosities which allow melt preparation of various materials such as fibers, sheets, etc.

Another embodiment of the invention also includes a trifunctional crosslinking compound which contains one to three benzylic hydroxyl functions and none to two primary or secondary aliphatic hydroxyl functions. All hydroxyl functions are either benzylic hydroxyl functions or primary or secondary aliphatic hydroxyl functions.

A further embodiment of the invention includes a tetrafunctional crosslinking compound containing from two to four benzylic hydroxyl groups and from none to two aliphatic and primary or secondary hydroxyl groups. All hydroxyl functions are either benzylic hydroxyl functions or primary or secondary aliphatic hydroxyl functions.

Definitions:

The term "backbone" or "polymer backbone" as used herein indicates the extended linear repeating chain of an oligomer or polymer.

A benzylic hydroxyl group is a hydroxymethyl ($-\text{CH}_2\text{OH}$) group substituted on a benzene ring, or a benzene ring containing other substituent groups.

A polyol with a high molecular weight useful according to the teachings of the invention typically includes polyester polyols represented by all of the below: Polyethylene butylene sebacate and the like; polybutylene adipate; polycaprolactone diol; aliphatic polycarbonate polyols such as those obtained by transesterification of polyhydroxyl compounds such as 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl(-1,3-propanediol, 1,8-octanediol and the like, with an aryl carbonate, for example, diphenyl carbonate; polyester polycarbonate polyols, for example reaction products of alkylene carbonates and polyester glycols such as polycaprolactone or products obtained by conducting a

reaction of ethylene carbonate with a polyhydric alcohol (such as ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol and the like; and polyether polyols represented by polytetramethylene ether glycol, polypropylene glycol, polyethylenepropylene glycol and the like.

5

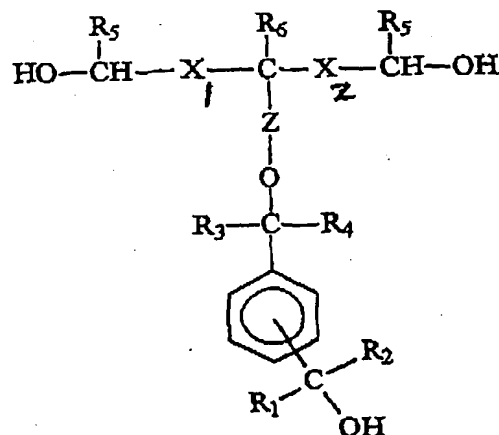
A polyol with a low molecular weight useful with the invention typically includes difunctional, trifunctional and tetrafunctional benzylic hydroxyl compounds as represented by 1,2-ethanediol; 1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 1,8-octanediol; 2,2-dimethyl-1,3-
10 propanediol and the like, and also 1,4-cyclohexanedimethanol; 1,4-bis(beta-hydroxymethoxy) benzene; 1,3-bis-(beta-hydroxyethoxy) benzene; 1,4-bis-(hydroxyethyl) ester of terephthalic acid; 1,3-bis(beta-hydroxyethyl) ester of isophthalic acid, and the like.

Additional polyisocyanates useful with the invention include: aromatic
15 diisocyanates such as 4,4'-diphenylmethane diisocyanate (MDI); 1,5-naphthalene diisocyanate' (NDI); 1,4-phenylene diisocyanate (PDI); 2,4 and 2,6-Toluene diisocyanate (commonly available as an 80/20 mixture of 2,4/2,6) and the like; benzylic diisocyanates such as TMXDI, p-xylylene diisocyanate, m-xylylene diisocyanate; aliphatic diisocyanates such as 1,6-
20 hexamethylene diisocyanate (HDI) and alicyclic diisocyanates such as 1,4-cyclohexane diisocyanate 4,4'dicyclohexylmethane diisocyanate, isophorone diisocyanate, and the like. Isocyanates with more than two isocyanate groups per molecule are also available and include the trimerized products of the simple diisocyanates listed above in which three isocyanate groups are
25 symmetrically located on an isocyanate nucleus, these are exemplified herein by the HDI Trimer (Tolonate[®]HDI) from Rhone Poulenc. There are also polyisocyanates with varying functionality greater than 2 from Upjohn, such as Isonate 143L and the PAPI series.

Typically, the difunctional benzylic hydroxyl compounds are used in the
30 polymer backbone to obtain special properties. Typically, the trifunctional and tetrafunctional benzylic hydroxyl compounds may be used both in the backbone of the polymer chains and in the crosslinks between neighboring

backbone or polymer chains. Useful difunctional benzylic hydroxyl compounds include: those in the benzene series represented by 1,4-benzenedimethanol, 1,3-benzene-dimethanol; and 1,2-benzenedimethanol; those in the pyridine series represented by 2,6-bis(hydroxymethyl)pyridine; those in the pyrazine series represented by 2,5-bis(hydroxymethyl)pyrazine; 2,3-bis(hydroxymethyl) pyrazine; and 2,6-bis(hydroxymethyl)pyrazine. Useful trifunctional benzylic hydroxyl compounds include those having one benzylic hydroxyl group and two primary or secondary aliphatic groups represented by Compound 1 and its analogues; those having three benzylic hydroxyl groups represented by 1,2,4-benzenetrimethanol; 1,3,5-benzenetrimethanol; and 2,4,6-benzenetrimethanol. Useful tetrafunctional benzylic hydroxyl compounds include those having four benzylic hydroxyl groups represented by 1,2,4, 5,-tetra(hydroxymethyl)benzene

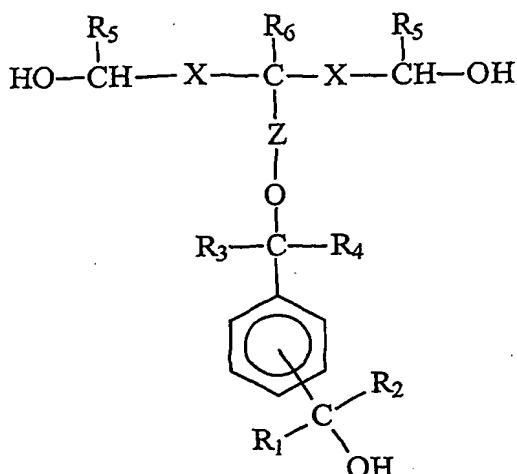
New compounds having a benzylic hydroxyl group useful for forming urethane and ester linkages are represented by the formula:



wherein R_1 and R_2 are identical or different and represent a group selected from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen groups; R_3 and R_4 are identical or different and represent a group selected from -H, and hydrocarbon groups containing up to ten carbon atoms; R_5 represents hydrogen, methyl, ethyl or propyl; R_6 represents hydrogen, methyl, or ethyl; ; X_1 (left arm), X_2 (right arm) and Z may be the same or

different and represent none (no additional segment present), methylene, ethylene, or p-phenylene; the benzylic hydroxyl moiety may be positioned in the para, meta or ortho position

Particularly useful benzylic hydroxyl compounds for making urethane bonds according to the present invention are represented by the formula:



wherein R_1 is H, and R_2 represents a group selected from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen groups; R_3 and R_4 are identical or different and represent a group selected from -H, and hydrocarbon groups containing up to ten carbon atoms; R_5 represents hydrogen, methyl, ethyl, or propyl; R_6 represents hydrogen, methyl, or ethyl; X and Z may be the same or different and represent none (no additional segment present), methylene, ethylene, or p-phenylene; the benzylic hydroxyl moiety may be any isomer in the para, meta or ortho position. Preferably the hydrocarbon groups of R_2 through R_4 are no more than five hydrocarbon groups and the benzylic hydroxyl moiety may be positioned in the ortho or para position, most preferably the para position.

These benzylic hydroxyl compounds have three functional groups, a reversible benzylic hydroxyl group available for crosslinking and two primary aliphatic groups available for incorporation into the polymer backbone. The compound owes its unique characteristics to the fact that the benzylic hydroxyl groups are more readily reversible than the aliphatic groups.

A polyisocyanate useful with the invention typically includes diisocyanates and other polyisocyanates. Diisocyanates are represented by isophorone diisocyanate (IPDI), TMXDI, phenylenediisocyanate (PDI), toluenediisocyanate (TDI), hexanediisocyanate (HDI); methylenediphenyldiisocyanate (MDI), naphthalene diisocyanate (NDI), and others disclosed US patent 4,608,418 to Czerwinski et al, which is hereby incorporated by reference. Additional useful isocyanates are disclosed in US patent 5,097,010 to Markle et al, which is hereby incorporated by reference.

Diols useful for making crosslinkers containing benzylic hydroxyl according to the invention include 1,2-ethanediol; propanediols represented by 1,2-propanediol or 1,3-propanediol; butanediols represented by 1,3-butanediol or 1,4-butanediol; pentanediols represented by 1,5-pentanediol; hexanediols represented by 1,6-hexanediol; and the like.

Triols useful for making crosslinkers containing benzylic hydroxyl groups according to the invention include 1,2,3-propanetriol (glycerin), 1,2,3- or 1,2,4-trishydroxybutane, and higher aliphatic triols with at least two of the hydroxyls in the 1,2- position.

Preferred crosslinking compounds containing benzylic hydroxyl groups useful with the invention typically include a tetrafunctional crosslinking compound containing from two to four benzylic hydroxyl groups and from none to two aliphatic and primary hydroxyl groups, and a trifunctional crosslinking compound containing from one to three benzylic hydroxyl groups and from none to two aliphatic and primary hydroxyl groups. A typical and preferred benzylic hydroxyl compound is 2-[[[(4-hydroxymethyl)benzyl]oxy]-1,3-propanediol (Compound 1).

The following examples and earlier examples are merely exemplary and illustrative of the invention and are not meant to limit the invention in any way.

EXAMPLE B1

This example illustrates a method for the preparation of a typical benzylic hydroxyl crosslinker useful with the invention. The method produces

a trifunctional crosslinking compound containing one benzylic hydroxyl group and two aliphatic and primary hydroxyl groups (2-[[4-hydroxymethyl]-benzyl]oxy}-1,3-propanediol - labeled as Compound 1). Compound 1 was synthesized for incorporation into the backbone of polyurethanes by using its aliphatic hydroxyl groups while leaving its benzylic hydroxyl group available to form reversible urethane-based crosslinks. Intermediate E was prepared to determine if blocking of the benzylic hydroxyl group by a readily removable group (a methoxyacetic acid ester) in Compound 1 was necessary to allow its appropriate incorporation into the urethane backbone. The synthetic route that was developed involves the initial synthesis of Intermediate E which was then deblocked to form Compound 1.

Preparation of Intermediate A

Intermediate A is composed of two isomers and is named as follows by IUPAC: cis- and trans-2-phenyl-1,3-dioxan-5-ol.

A one liter, three neck, round bottom flask was equipped with a Barrett tube attached to a reflux condenser which was attached to an argon inlet via a mineral oil bubbler. This flask, which contained a magnetic stir bar and was positioned in a heating mantle, was flushed with argon and then charged with 200 ml of benzene, 160.0 grams (1.51 moles) of benzaldehyde, 150.0 grams (1.63 moles) of glycerin and 1.00 grams of p-toluenesulfonic acid monohydrate. A blanket of argon was kept over the flask during the reaction period. The reaction mixture was refluxed until close to the theoretical amount of water had collected in the Barrett tube and transferred to a one liter separatory funnel. One hundred ml of 0.1M sodium hydroxide was added to achieve pH 9-10 and the mixture was extracted with 350 ml of diethyl ether. The ether extract was first treated with a saturated solution of sodium hydrosulfite (32.75 grams/ 100 ml water) causing the formation of some solid in the ether layer, then washed with water (150 ml), followed by a 5% sodium bicarbonate (100 ml) treatment. After a water wash (2 x 150 ml), the ethereal layer was dried over sodium sulfate overnight. The solvent was stripped on a rotating evaporator (bath at 30C) to obtain 199.70 grams of

liquid. This material was dissolved in 400 ml low boiling petroleum ether and refrigerated to give a solid which weighed 186.28 g after filtration and drying under vacuum. Since proton NMR analysis indicated that a significant amount of benzaldehyde was still present, this material was dissolved in diethyl ether (800 ml) and washed with 2 x 125 ml of sodium hydrosulfite (61.0 grams in 200 ml water). The white solid that formed during this period was dissolved by the addition of 100 ml of water. The ether layer was washed with 5 x 120 ml water (pH 2), passed through cotton, dried over sodium sulfate overnight, and then stripped to obtain a yellow-orange liquid (139.1 grams). This material produce a low melting solid when placed in a refrigerator. When brought to ambient temperature, the liquid phase was decanted and the remaining solid was dissolved in a total of 400 ml of dry toluene at room temperature. After addition of 400 ml of hexane, a copious amount of white solid precipitated at room temperature. After this mixture was placed in a refrigerator overnight, a fine white solid was filtered and dried which weighed 74.33 grams (27.4% yield).

Sodium bisulfite can also be used to advantage in removing unreacted benzaldehyde. The procedure for this reaction is found in: C. Piantadosi, C.E. Anderson, E.A. Brecht and C.L. Yarbrow, J. Am. Chem. Soc., 80, 6613-6617 (1958).

The proton and carbon-13 nuclear magnetic resonance (NMR) spectra of this material indicated that it was a mixture of cis- and trans-1,3-benzylidene glycerin and that 1,2-benzylidene glycerin had been completely removed by recrystallization.

Preparation of Intermediate B

Intermediate B is composed of tow isomers and is named as follows by IUPAC: cis- and trans-5-{[4-bromomethyl)benzyl]oxy}-2-phenyl-1,3-dioxane.

A two liter, three neck, round bottom flask equipped with an argon inlet and mechanical stirrer was first flushed with argon and then charged with 1167 ml dimethylsulfoxide (dried over molecular sieves) and 26.10 grams powdered potassium hydroxide (0.466 moles). This mixture was stirred for

five minutes and then 21.00 grams 1,3-benzylidene glycerin (0.1165 moles) was added followed by addition (all at once) of 92.26 grams α,α' -dibromo-p-xylene (0.3495 moles). The lemon yellow reaction mixture was stirred while maintaining it under an argon blanket (via a mineral oil bubbler) for an additional eighty minutes at ambient temperature.

The reaction mixture was then added to a six liter separatory funnel containing 250 grams of ice and 2250 ml of water and considerable yellow solid formed at this point. The aqueous layer was extracted with methylene chloride (a 2000 ml portion followed by 2 x 1300 ml portions). The combined organic layers were split in half, filtered through cotton to remove the yellow solid, and each half was washed with 3 x 1800 ml water. The methylene chloride was passed through a cotton plug and dried over sodium sulfate. The solvent was stripped on a rotating evaporator and the resulting solid was dried in a vacuum oven with phosphorous pentoxide to obtain 88.50 grams yellow solid. The excess α,α' -dibromo-p-xylene was removed by sublimation and the residue was used directly to prepare Intermediate C (see below). To illustrate, one sublimation was performed with 52.43 grams crude Intermediate B in a large sublimation chamber requiring dry ice within the cold finger. This apparatus was maintained at 0.035 Torr and 80°C in a controlled temperature oil bath for a total of 47.5 hours until minimal further sublimate was formed. The residue (non-sublimed material) weighed 13.83 grams (26.4 % of the starting weight).

The proton NMR spectrum of this material indicated the presence of both trans- and cis-Intermediate B. Preparative scale High Performance Liquid Chromatography (HPLC) was used to fractionate this mixture (using a normal phase HPLC column with tetrahydrofuran (THF)/isooctane (15:85)) to obtain these isomers in a pure state whose structures were confirmed by proton NMR spectroscopy and gas chromatography/mass spectroscopy (GC/MS) (in the electron impact mode).

Preparation of Intermediate C

Intermediate C is composed of two isomers and is named as follows by IUPAC: cis- and trans-4-{[(2-phenyl-1,3-dioxan-5-yl)oxy]methyl}benzyl methoxyacetate.

5 Potassium methoxyacetate was prepared by dissolving 52.47 grams methoxyacetic acid (0.5800 moles) in 150 ml of distilled water in an Erlenmeyer flask and initially adding 32.50 grams potassium hydroxide (nominally 0.580 moles). Addition of 2 drops of a 1% ethanolic phenolphthalein solution indicated that the end point had not been reached,
10 so this solution was titrated with a 10 % aqueous solution of potassium hydroxide until a pink color persisted. This solution was freeze dried and dried further in a vacuum oven, in the presence of phosphorous pentoxide, to yield 71.94 grams of a white solid.

A 300 ml, three neck, round bottom flask containing a magnetic stir
15 bar and equipped with a reflux condenser and gas inlet tube was positioned in a heating mantle and flushed with argon. This flask was maintained under an argon blanket using a bubbler filled with mineral oil. The flask was charged with 0.9147 grams 18-crown-6 (3.461 mmoles) and 134 ml acetonitrile was transferred from an anhydrous source using syringe techniques. Potassium
20 methoxyacetate (18.85 grams; 0.1471 moles) was added and the milky white suspension was stirred at ambient temperature for 50 minutes to allow coordination of the 18-crown-6 with the potassium ion. Crude Intermediate B (26.75 grams and 0.07364 moles) was added and the yellow mixture was refluxed for 110 minutes. After cooling slightly, the mixture was filtered
25 through a Buchner funnel (Whatman # 1 paper) and the filter cake was washed with 4 x 50 ml acetonitrile and then with 3 x 50 ml benzene. This washing was performed to remove residual Intermediate C from the filter cake. The filtrate was stripped on a rotating evaporator and the resulting material was placed in a vacuum oven containing phosphorous pentoxide to
30 obtain 29.15 grams of a brown solid.

Column chromatography was used to purify Intermediate C. A column having an internal diameter of approximately 7.5 cm was filled with 292

grams of silica gel slurried in excess benzene. Crude Intermediate C (29.15g) was dissolved in 155 ml of benzene and applied to this column using benzene as the eluent. A total of 19 fractions were collected ranging in size from 125 ml to 250 ml for fractions 1-7 and 300 ml to 500 ml for fractions 8-19. These fractions were stripped on a rotary evaporator and dried overnight at ambient temperature in a vacuum oven in the presence of phosphorous pentoxide to obtain a total of 11.41 grams in total fraction weight. Select fractions were analyzed by gas chromatography (GC) and by gel permeation chromatography (GPC). GC results indicated that Intermediate C was the major component. GPC analyses indicated that Intermediate C and Byproduct D were present in all fractions but the relative ratio of Intermediate C steadily increased with increasing fraction number. Thus, the latter chromatography fractions afforded Intermediate C in highest purity containing the smallest quantities of Byproduct D. Byproduct D is composed of several isomeric forms and is named as follows by IUPAC: (cis, cis-); (cis, trans-); or (trans, trans)-bis-1,4-[[(2-phenyl-1,3-dioxan-5-yl)oxy]methyl]benzene.

Preparation of Intermediate E

Intermediate E is named as follows by IUPAC: 4-[[(2-hydroxy-1-(hydroxymethyl)ethoxy]methyl]benzyl methoxyacetate.

Fractions 6-15 from Intermediate C (8.15 grams) obtained by column chromatography (described above) were transferred to a one liter Morton flask equipped with a mechanical stirrer and 489 ml of 90/10 (v/v) acetic acid/water were added. After stirring for thirty minutes, an additional 81.5 ml of acetic acid/water (90/10) was added. After stirring rapidly for 18.5 hours at ambient temperature, a sample was removed which was found to be depleted in Intermediate C by proton NMR spectroscopy. After the reaction mixture had been stirred approximately 22 hours, the material was stripped on a rotary evaporator with vacuum pump pressure using a bath temperature of approximately 34°C. Portions of acetonitrile were added to aid the removal of residual acetic acid and water by azeotropic distillation. The resulting

material was dried further at ambient temperature in a vacuum oven using a vacuum pump to obtain 6.25 grams of a yellow solid.

Byproduct F was found to be present. Byproduct F is named as follows by IUPAC: bis-1,4-{[2-hydroxy-1-(hydroxymethyl)ethoxy]methyl}benzene was

5 found to be present. In order to remove Byproduct F, this material was magnetically stirred with 345 ml methylene chloride for three hours and this mixture was then filtered through a 0.45 micron filter. The filter cake was washed with methylene chloride and dried at ambient temperature under high vacuum to give 0.975 grams Byproduct F. The proton and carbon-13 NMR
10 spectra of Byproduct F were in agreement with its structure. The filtrate was stripped to give 5.09 grams material which was determined by GC (after trimethylsilylation with trimethylsilyl chloride and hexamethyldisilazane in pyridine) to contain 85.8 % Intermediate E and 2.8 % Byproduct F, with the remainder being unknown components (percentages express the relative area
15 percentages of GC peaks). The proton and carbon-13 NMR spectra, infrared (IR) spectrum, and GC/MS spectrum (after trimethylsilylation with trimethylsilyl chloride and hexamethyldisilazane in pyridine) were in agreement with the structure of Intermediate E.

The entire procedure described above for hydrolysis of Intermediate C
20 was repeated with Fractions 16-19 of impure Intermediate C (1.07 grams) obtained from the same column chromatography described above. Using essentially the same procedure described above in a scaled fashion, 0.72 grams of a product was obtained that was indicated by GC analysis (after trimethylsilylation) to contain 92.2 % Intermediate E and 1.5 % Byproduct F,
25 with the remainder being unidentified.

These fractions were purified by recrystallization from isooctane/THF solvent mixtures which led to only small reductions in Byproduct F in low recrystallization yields. However, semipreparative HPLC, using a normal phase column and gradients of isooctane and THF as the mobile phase, gave
30 Intermediate E in which Byproduct F was reduced to below detectable limits (determined by GC after trimethylsilylation).

Preparation of Product Compound 1

Compound 1 is named as follows by IUPAC: 2-{{4-(hydroxymethyl)benzyl}oxy}propane-1,3-diol.

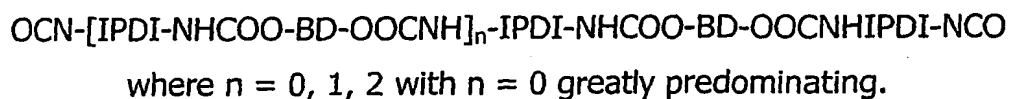
Intermediate E (0.558 grams) was dissolved in 10 ml dry methanol (distilled in glass) and this solution was transferred to a thick walled glass bottle containing a magnetic stir bar. After bubbling argon through this solution for 15 minutes to remove dissolved oxygen while cooling the solution to 0 C, ammonia gas was bubbled into this solution through a hypodermic needle for approximately 0.5 hour. The ammonia gas was initially passed through a tower of sodium hydroxide pellets to remove residual water from the gas. The bottle was then capped with a TeflonTM-lined crown seal and allowed to stir for ten hours while warming to ambient temperature. The bottle was then opened and the ammonia was removed by an argon purge. The methanolic solution was then stripped in a rotary evaporator to obtain a brown gummy solid.

This solid was dissolved in approximately 0.5 ml dry methanol and approximately 5 ml dry diethyl ether was added. The solution became turbid after storing overnight in a freezer at approximately -30°C and a crystalline solid formed. The supernatant liquid was decanted and the solid was washed with ether and dried under vacuum to obtain 0.164 grams yellow-white crystalline solid. The proton NMR spectrum of this material was in accord with the structure of Compound 1 but GC analysis (after trimethylsilylation) indicated this material to be only approximately 80 % pure. This once-recrystallized material was then recrystallized two more times from 10/1 (v/v) diethyl ether/methanol to obtain a white crystalline material. Proton and carbon-13 NMR spectra obtained from the second crop were in accord with the structure of Compound 1. Two crops of crystals were obtained from the third recrystallization, the first crop weighing 71 mg and the second crop weighing 35 mg. GC analysis of the first crop (after trimethylsilylation) indicated that this material was approximately 97 % pure with one slightly later eluting peak representing approximately 2 % of the total peak area.

The proton NMR spectrum of the first crop was essentially identical to the spectrum of the second crop obtained by recrystallization described above.

EXAMPLE C1 - Crosslinker Making

5 This example illustrates a method for making an isophoronediiisocyanate capped 1,4-butanediol (IPDI-BD-IPDI) crosslinker useful with the invention. The acronym IPDI-BD-IPDI is used to represent a structure more completely described as



Vacuum distilled (center cut), dry, 1,4-butanediol (BD, Aldrich 24,055-9), 4.5 g (0.050 mole) was added to a previously flame dried, and cooled
15 while flushing with dry argon, 2 liter Pyrex Erlenmeyer flask. A tared 1000 ul, Teflon plunger, microsyringe was used for transfer. Dry chloroform (CHCl_3 , Burdick and Jackson B&D, distilled in glass, 478.4 g, 318.9 cc) was added to the BD using a flame dried 1-liter Pyrex graduate while a mild argon flush was maintained. About 20 grams of Fluka nondusting 3A molecular sieve was
20 added to the solution to ensure that no water was present or picked up. Separately a 2-liter, three-neck (standard taper size 24/40 necks) reaction flask containing a football-shaped Teflon coated magnetic stir bar was flame dried and cooled while flushing with dry argon. The flask and stir bar were then tare weighed (296.16 g) and clamp mounted on a rack in a fume hood
25 for conducting the reaction. A 1-liter Pyrex dropping funnel with a bottom 24/40 male joint and a drip tip, and a pressure equalizing side arm, was placed into one of the side 24/40 female joints. A pre-flame-dried, water cooling equipped reflux condenser was placed in the other side joint. The assembled apparatus was all re-flame-dried and cooled while argon flushing.
30 The argon was passed through the top of the dropping funnel, which had a side-arm gas inlet adapter affixed, through the reaction flask, and exited from a gas outlet adapter at the top of the water cooling equipped condenser. The

outlet gas was then passed through a mineral oil bubbler to allow adjustment and visual observation of the gas flow rate. The center port of the reaction flask was closed with a 24/40 stopper. Then, the reaction flask assembly was removed from its mounted position on the rack, while maintaining a slow argon flush, and 222.5 g (1.00 Mole) of center cut vacuum distilled isophorone diisocyanate (Aldrich 31,62-4, IPDI) was added to the unmounted reaction flask assembly, which was placed on a large torsion balance to accurately weigh the IPDI. The IPDI was poured from the argon flushed 1 liter Pyrex round bottom distillation receiver into which it had been distilled (under argon in a flame dried Pyrex distillation assembly). The theoretical yield of IPDI-BD-IPDI crosslinker was calculated to be 26.9 g (0.0105 Mole BD x 538.74 g/Mole molecular weight of the expected IPDI-BD-IPDI product).

Similarly 167 grams (111cc) of dry B&D CHCl_3 solvent was added to the reaction flask and the assembly was then remounted on the rack in the hood. Then the separately prepared BD in CHCl_3 solution (Erlenmeyer flask) was transferred directly to the dropping funnel and rinsed in with three small portions (~10 cc each) of CHCl_3 to insure that all BH was transferred, leaving the Fluka 3A molecular sieve in the 2 liter Erlenmeyer flask. The reaction flask was then heated to 50°C using a thermostatically temperature controlled mineral oil bath mounted on a lab jack, which was raised until the preheated mineral oil level was well above the level of the magnetically stirred clear, colorless IPDI/ CHCl_3 solution. The CHCl_3 solvent quickly boiled and refluxed gently. The CHCl_3 /BD solution in the dropping funnel was then added in rapid-dropwise fashion over a 2.5 hour period, while maintaining a steady, slow (1 bubble per 2 or 3 seconds) argon purge. The reaction was maintained at 50°C for 24 hours after BD addition was complete. Then the heat was turned off and the reaction mixture cooled to ambient temperature by removing the 50°C mineral oil bath and letting the mixture stand over the weekend, while maintaining the slow argon purge. The CHCl_3 was then vacuum distilled (stripped) from the reaction flask, while stirring was maintained, by replacing the reflux condenser with a vacuum pump connected through a large capacity, dry ice cooled, trap to collect the

distillate. The dropping funnel was also removed and replaced with just the argon inlet adapter. Argon flow was adjusted to nil when vacuum was applied. The mineral oil bath was replaced around the reaction flask and heated only very slightly to maintain a temperature near ambient (~ 25-27°C). The CHCl_3 was stripped carefully, to avoid foaming, until 175.9 g of a fairly thin, clear, very light yellow, presumably CHCl_3 free liquid was obtained. Apparently 51.1 g of IPDI had codistilled with CHCl_3 since the total weight of BD + IPDI originally was 227.0 grams.

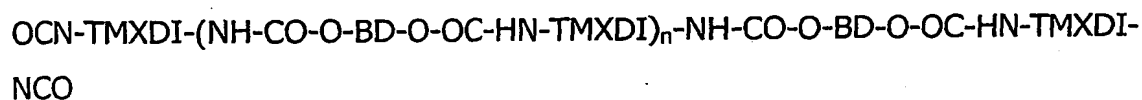
One (1.0) gram of the liquid product was added to 25 cc of bone-dry hexane (Aldrich 22,706-4, water < 0.002%) in a dry 100 cc Pyrex Erlenmeyer flask to test the use of hexane as a purifying medium. A white, emulsion-looking, mixture was obtained, which separated after several hours into a thin layer of clear viscous liquid on the bottom and a clear, colorless upper layer. Since IPDI is very soluble in hexane and the product, with two internal, highly hydrogen bonding urethane bonds, was expected to be hexane insoluble, it was assumed that the thin bottom layer was the desired product and the upper layer was a hexane solution of unreacted IPDI. Hence, the entire batch of product was added to a total of 3.6 liters of the dry hexane in two equal portions in two liter, flame-dried, Pyrex Erlenmeyer flasks. The same precipitation phenomenon occurred on the larger scale. After phase separation was complete the clear, supernatant hexane-IPDI layers were decanted, and the viscous, clear, but very slightly yellow product layers were rinsed with about 50 cc of dry hexane, the product redissolved in about 10 cc of bone dry methylene dichloride (CH_2Cl_2) (Aldrich 27,099-7, < 0.005% water) and reprecipitated with about 200 cc of dry hexane in each flask. When phase separation was complete, this dissolution and reprecipitation process was repeated.

The two product portions were then combined into a 100 cc, flame dried, one neck, Pyrex round bottom flask using several small (~ 10 cc) amounts of the bone dry CH_2Cl_2 solvent. The CH_2Cl_2 was carefully stripped in a vacuum oven at ambient temperature, then dried overnight in the vacuum oven (~ 1 Torr) with mild heating (~ 35°C). Obtained were 11.87 grams of a

clear, very light yellow, extremely viscous oil or liquid. This was a 44.1% yield based on the theoretical yield of 26.94 grams. A significant portion of the product was apparently removed during the hexane precipitation purification process. This should be recoverable by, for example, separate vacuum distillation of the unreacted IPDI, after distilling all of the precipitation medium hexane. Although this was not done, it is considered very likely that the hexane and unreacted IPDI could be collected and recycled, and virtually all of the product IPDI-BD+IPDI crosslinker product recovered, if this is desired. The product was analyzed by H-NMR. The product spectrum was compared with the HNMR spectra of the starting IPDI and BD. The spectra of all three materials are fully consistent with the expected HNMR spectra.

EXAMPLE C2 Crosslinker Making

This example illustrates the dibutyltindilaurate catalyzed preparation of TMXDI capped 1,4-butanediol crosslinker (TMXDI-BD-TMXDI). This acronym (TMXDI-BD-TMXDI) is understood to represent



where $n=0,1$, or 2 with $n=0$ greatly predominating.

The same two liter reaction flask, magnetic stir bar and handling and flask drying procedures were used as in Example C1. Thus, 244.3 grams (1.000 mole) of as received 1,3-bis(1-isocyanato-1-methyl-ethyl) benzene (TMXDI, CYTEC Industries) were added to the dried and argon flashed reaction flask. Then 4.506 grams (0.050 moles) 1,4-butanediol (BD) were added. The two reactants were immiscible. Then 100 grams (127 cc) anhydrous acetonitrile (Aldrich 27,100-4, water < 0.001%) were added to the flask and a clear, colorless, one phase, reaction mixture was quickly obtained. Then 0.0365 grams (6.115×10^{-5} mole) of dibutyltindilaurate catalyst were added. This is 0.122 mole percent of catalyst based on the 0.050 moles of BD present. The clear, thin mixture was then stirred at ambient temperature

(~ 23°C) under a constant argon flush for 9 days. The acetonitrile solvent was then vacuum stripped at ~ 23-25°C using the mineral oil bath and a very low heat input. After distillation ceased, 211 grams of a clear, slightly viscous solution of the TMXDI-BD product dissolved in unreacted TMXDI were
5 obtained. This is 37.8 grams less than the expected weight of 248.8. Presumably this amount of TMXDI co-distilled with the acetonitrile. The theoretical amount of TMXDI-BD-TMXDI product present, if no dimerization, trimerization, or higher oligomerization occurred, was 28.94 grams. Hence, the percentage by weight of expected product in the final mixture was
10 $(28.94/211.4) \times 100 = 13.69\%$. A 30.0 gram aliquot of the final mixture was taken for product recovery and purification. The theoretical yield of TMXDI-BD-TMXDI product from this aliquot was $(0.1369 \times 30.0) = 4.11$ grams.

The solution was added to 300 grams (455 cc) of the anhydrous, reagent grade hexane in a dry 500 ml Erlenmeyer flask, under argon. As in
15 Example C1, a white, emulsion-like suspension was obtained, which gradually separated into two distinct phases. These were a thin layer of clear, viscous liquid on the bottom of the flask and a large amount of clear, thin supernatant liquid. This upper layer consisted of hexane and presumably most of the unreacted TMXDI, which is readily soluble in hexane, as well as some portion
20 of the product codissolved in the hexane/TMXDI mixture. It was decanted and the thin, clear product layer rinsed with about 10 cc of anhydrous hexane twice. The viscous, clear, colorless liquid was redissolved in about 10 cc of dry methylene chloride (CH_2Cl_2) and reprecipitated in 100 cc anhydrous hexane as before. The supernatant layer was decanted, the viscous, clear
25 product washed with 10 cc hexane and again dissolved in 10 cc CHCl_3 and precipitated in 100 cc anhydrous hexane. The final supernatant layer was decanted, the product layer rinsed with more of the anhydrous hexane and the product vacuum dried overnight at ~ 1 Torr and 30-35°C to obtain 3.15 grams of clear, practically solid, colorless product. This was 76.6% overall
30 yield based on a theoretical 4.11 grams of product from the aliquot. H-NMR analysis of this three times precipitated product indicated 99+% purity.

EXAMPLE C3

4-Hydroxymethyl-beta-(hydroxyethoxy)benzene, hereafter referred to as Compound G, is reacted with MDI in a mole ratio of two moles of compound G and one mole of MDI. This constitutes an equimolar ratio of aliphatic primary hydroxyl and isocyanate groups. The reaction is carried out by melting together under anhydrous and air-excluded conditions the two component reactants. They are heated while stirring and kept under a very slow purge of inert gas such as dry nitrogen or dry argon. They are heated to a temperature of at least about 180°C and perhaps beneficially to a temperature of about 200°C. After maintaining this temperature for about 10-30 minutes, the mixture is cooled slowly to the temperature at which the mixture solidifies. This will be done over about a 30-60 minute time period. Obtained will be the bis-hydroxymethyl-capped-diurethane coupled product from the formation of stable urethane bonds between the two primary aliphatic hydroxyethyl groups and the two MDI isocyanate groups. The benzylic hydroxyl groups will be essentially uncombined and will constitute the end of groups of this bis-urethane.

EXAMPLE C4

Compound G of the previous example is reacted with the tri-isocyanate compound available commercially. This compound is Compound H from Rhone-Poulenc known as Tolonate® (HDT) Trimer. Compound G is reacted with Compound H in a mole ratio of three moles of Compound G and one mole of Compound H. This constitutes an equimolar ratio of aliphatic primary hydroxyl and isocyanate groups. The reaction is carried out following the procedure of Example C3 obtained will be the tris(hydroxymethyl)-capped-tri-urethane coupled product obtained from the formation of stable urethane bonds between the three primary hydroxyethyl groups of Compound G and the three isocyanate groups of Compound H. The three benzylic hydroxyl groups will be essentially uncombined and will constitute available reactive groups for the formation of reversible urethane crosslinking bonds when combined in a minor amount (less than or equal to 50 mole percent of the

hydroxyl groups used) polymer with a major amount (less than or equal to 50 mole percent of the hydroxyl groups used, from di-benzylic hydroxyl compounds or oligomers such as 1,4-benzenedimethanol and/or the di-hydroxymethyl compound product of Example C3.

5

EXAMPLE P1 Polymer Making

A control polyurethane was prepared without using any Compound 1. Diphenylmethane diisocyanate, commonly referred to as methylenediphenyl-diisocyanate (MDI), polybutylene adipate (PBA) with a molecular weight of
10 about 1986 (a high molecular weight polyol with two end group aliphatic-hydroxybutyl-hydroxyl groups), and 1,4-butanediol (BD) were used. The MDI and BD were reagent grade chemicals obtained from Aldrich (MDI, Aldrich 25,643-9; BD, Aldrich 24,055-9) but were vacuum distilled before use. The PBA is a commercially available polyurethane polymerization quality aliphatic
15 polyester diol. All reactants were handled under dry argon gas. The polymerization was performed in a silylated Pyrex reactor tube (~50 cc heavy walled test tube) equipped with a standard taper 24/40 top joint. Silylation of the Pyrex glass surface was carried out using an octadecyltrialcoxysilyl functionalized silane (Siliclad®), Gelest Product No. SIS 6952-0, lot-964-3014,
20 20% active). A 1% solution of this product is made up in distilled water. The glass is rinsed with 5% aqueous NaOH followed by several distilled water rinses, then the 1% Siliclad®. It is then rinsed with water again and dried at about 100°C for one hour to provide an extremely stable hydrophobic surface. A simple head adapter with a small opening on top just large enough for a
25 thin stainless steel spatula to fit through, and a side argon inlet tube, was placed in the top standard taper joint during the polymerization. The head adapter was removed from the Pyrex reaction tube and 8.937 grams (4.50 mMole) of PBA and then 2.463 (9.842 mMole) of MDI were weighed into the dry (silylated) tube. The head adapter was reinstalled and an argon flush was
30 immediately started. The tube was lowered into a Woods metal bath preheated to 97°C. The contents melted and were carefully stirred at 90-100°C for one hour. Care was taken not to splash any reaction mixture on

the upper walls of the tube. A moderate viscosity increase occurred during the one hour of heating, with essentially all of the increase occurring in the first 30-45 minutes.

Then 0.4908 g (5.446 mMoles) of 1,4-BD was quickly added directly
5 onto the top of the melt via a pre-tared 1000 ml syringe while maintaining the argon flush. The Woods metal bath was then heated rapidly to approximately 200°C while stirring was continued. The heat up from 100°C to 200°C only required about 6-7 minutes. Stirring was continued while heating at 197-200°C for about 30 minutes. During the first 10-15 minutes of this period the
10 melt viscosity increased rapidly until a quite viscous but still readily hand stirrable melt was obtained. This melt viscosity did not noticeably change over the last 10-15 minutes of stirring at 197-200°C. A fiber was drawn from this melt. The fiber was quite strong and elastic at room temperature. The hot molten polymer was then rapidly removed from the small reaction vessel,
15 into a Teflon dish, and allowed to cool. The product was a tough, strong elastic thermoplastic.

A post polymerization treatment to insure that polymerization was complete was carried out by heating the polymer mass overnight at 80°C in a vacuum oven set at about 1 Torr.

20 The product, both before and after this vacuum oven treatment was a strong, tough, elastic thermoplastic. A small piece readily dissolved in dry dimethyl formamide (DMF) in several hours at room temperature. A small piece was also submitted for gel permeation chromatography (GPC) molecular weight analysis. This was done using a Waters GPC instrument and columns
25 with tetrahydrofuran (THF) solvent. The GPC was calibrated using four narrow molecular polystyrene standards. The GPC molecular weight of a commercial Spandex-type, melt processible, elastic thermoplastic polyurethane was also measured at the same time. The number (M_n), peak (M_p), and weight M_w average molecular weights for the commercial TPU are,
30 respectively, $M_n=57,539$; $M_p=126,884$; and $M_w=147,283$. The same molecular weight data for the laboratory prepared control TPU are, respectively, $M_n=52,200$; $M_p=131,525$; and $M_w=144,381$. This shows that a

TPE based on an aliphatic polyesterdiol, MDI and 1,4-Butanediol can readily be carried out to make a polyurethane with molecular weight parameters within a few percent of those desired in a commercial product.

5 EXAMPLE P2

This example illustrates the production of a thermoplastic polyurethane elastomer (TPE) with pendant benzylic hydroxyl groups using Compound 1.

The polymerization was performed in silylated Pyrex reaction tubes (~50 cc volume) equipped with 24/40 joints and using a molten Woods metal bath for heating. A 24/40 adapter with an argon inlet was inserted into the top of the Pyrex reaction tube. Dry argon was slowly, but constantly, flushed through a small opening in the reactor tube during the reaction. The reaction mixture was stirred with a thin stainless steel spatula inserted through a small opening in the top of gas inlet adapter. Constant, slow stirring was performed due to the small scale used and the requirement that ingredients be mixed but not spread upward on the tube surface. This assured that all material was available for reaction.

Next, 2.2343 grams (1.125 m Mole) of polybutylene adipate (MW=1986, Eq. wt. =993) and 0.6356 g (2.540 mMole) of MDI were weighed to four decimal places directly into the reaction tube using an analytical balance placed in a glove bag which was flushed and filled with argon. All reactants were carefully placed onto the bottom of the reaction tube. The reactor tube was then removed from the glove bag with the head adapter already in place the mixture was heated while stirring at 100-110°C for one hour during which time it became moderately viscous. The reaction tube was lifted just out of the molten metal bath, which was then heated rapidly up to 197-200°C. Then, 0.1177 g (1.3063 mMole) of 1,4-BD was quantitatively carefully added directly onto the still argon flushed prepolymer mixture from a preweighed 1000 microliter syringe, which was also reweighed after addition of 1,4-BD to insure accurate weight addition by difference. Immediately after this 0.0146 g (0.0688 mMole) of Compound 1 was added, also carefully placing it on top of the reaction mixture. The end capper, diethyleneglycol

ethyl ether, 0.0107 g (0.0797 mMole) was then added from a microsyringe, again weighing the syringe before and after the addition. These additions were performed while maintaining the argon flow. As soon as the additions were complete, the reactor tube was lowered back into the Woods metal bath and the mixture was heated at 197-200°C while carefully stirring for 30 minutes.

The total hydroxyl content of the reaction mixture was 5.0793 mMole, while the total isocyanate content was 5.0796 mole. The Compound 1 hydroxyl content represented 5 mMolar % replacement of butanediol mMolar hydroxyl content. Table 3 shows the quantities of all components used to prepare the polymer.

Table 3

Component	Weight (g)	Component Amount (mMole)	Hydroxyl Amount (mMole)	Isocyanate Amount (mMole)
PBA ^a	2.2343	1.125	2.250	0
MDI	0.6356	2.540	0	5.0796
1,4-BD	0.1177	1.3057	2.6115	0
Compound 1	0.0146	0.0688	0.1376 ^b	0
End Capper ^c	0.0107	0.0797	0.0797	0
Total:	3.0129	N/A	5.0788	5.0796

a - polybutyleneadipate

b - this number of moles includes only the two primary hydroxyl groups and not the benzylic hydroxyl group

c - diethylene glycol ethyl ether (MW=134.18; dried over Fluka 3A molecular sieves.

EXAMPLE P3

The reactor tube of Example P2 was then removed from the hot Woods metal bath and 2.2250 g of the thermoplastic polyurethane elastomer

with pendant benzylic hydroxyl groups was removed (73.85% of the calculated total weight of 3.0129g), thus leaving a calculated quantity of 0.7878 g of the thermoplastic polyurethane (26.15%) (TPE) with (presumably mostly unreacted) pendant benzylic hydroxyl groups in the reaction tube.

5 This polymer contained a calculated quantity of 0.0180 mMole of Compound 1. Great care was taken while removing this control polyurethane portion of Example P2, to not leave any polymer deposits on the walls of the reactor tube, above the polymer melt line. A crosslinker made from an excess of isophorone diisocyanate with 1,4-butanediol (with a presumed IPDI-BD-IPDI
10 structure; molecular weight = 534.7, from Example C1 was then added to the melt in an amount based on the presumed presence of 90% of the theoretical amount of benzylic hydroxyl groups. This quantity corresponded to $0.90 \times (0.0180/2) = 0.0081$ mMole or 4.3 mg crosslinker, which was carefully added to the top surface of the remaining melt. The total quantity of MDI derived
15 carbamate groups in the TPE remaining in the reactor tube was $5.08 \times 0.2615 = 1.33$ mMoles. It should be noted that the maximum quantity of urethane groups derived from the benzylic hydroxyl groups of Compound 1 and the IPDI-based crosslinker (0.0081 mMole) was $2 \times 0.0081 \times 100 = 0.0162$ mMole of urethane groups. This quantity of urethane groups corresponds to
20 1.20% of the total urethane groups in this sample $0.0162 \text{ mMole} \times 100 / (1.33 \text{ mMole} + 0.0162 \text{ mMole}) = 1.20 \%$. The reactor tube was then placed back in the molten metal bath (maintained at about 200°C) and the crosslinker was very carefully and thoroughly mixed into the quite viscous melt over a five minute period.

25 The viscosity of the molten polyurethane was essentially the same as the final melt viscosity of the control TPU in Example P1 and the experimental TPU product final melt viscosity in Example P2, both before and after adding the IPDI-BD-IPDI crosslinker. Hence essentially no crosslinking was in evidence at the 200°C reaction temperature.

30 This product, a quite viscous but still readily hand-stirrable melt, was then cooled. Very importantly, a small piece of this material when placed in dimethylformamide (DMF) at ambient temperature swelled slightly over 3-4

hours. It did not change (swell) any additional amount after 24 hours more at room temperature. The fact that it did not dissolve showed that it was crosslinked, as desired. In contrast, the control material, which was removed from the reactor tube before the isophorone-based crosslinker was added, dissolved readily in DMF over a 3-4 hour period at ambient temperature. The solution was clear and qualitatively free of gel (i.e. undissolved polymer). This showed that it was not crosslinked. These solubility test results provide strong evidence that Compound 1 was largely copolymerized into the hard segment of the backbone structure of the TPU with pendant benzylic -OH groups that were largely not reacted with isocyanate groups, until the IPDI-BD-IPDI crosslinker isocyanate groups were added. Interestingly then, when the crosslinked TPE was reheated back to 200°C under argon gas, fibers could readily be drawn from the melt. These fibers were quite strong and elastic at room temperature. Films were then prepared from both the IPDI-crosslinked material and the control material by pressing these materials between sheets of Teflon in a heated press (at 200-300 lbs. of force at about 180-190°C). Thin clear, tough, elastic films having a thickness of 1-2 mils were readily obtained. These films were used for the IR reversion studies described below.

Although the control material appeared to completely dissolve in dimethyl formamide (DMF) it is believed that a small number of crosslink sites were made with the material of Compound 1. It is noted that there was an excess of 0.0008 mMole of isocyanate added. Due to the ratios of the materials added, however, the number of crosslinked sites was too small to interfere with apparent solubilization of the polymer.

EXAMPLE P4

This example illustrates the production of a reversible thermoplastic polyurethane elastomer (TPE) but which contains, at room temperature crosslinked MDI urethane bonds, by using Compound 1 at 5 mole percent replacement of 1,4-BD and an amount of MDI sufficient to provide an isocyanate content that is equivalent to the total hydroxyl content, including

the benzylic hydroxyl content. The benzylic urethane crosslinks will be present at room temperature and up to at least about 150°C, but will reverse when heated above this temperature to about 200°C, allowing the TPE to melt

5 The polymerization is performed in silylated Pyrex reaction tubes (~50 cc volume) equipped with 24/40 joints and using a molten Woods metal bath for heating. A 24/40 adapter with an argon inlet is inserted into the top of the Pyrex reaction tube. Dry argon is slowly, but constantly, flushed through a small opening in the reactor tube during the reaction. The reaction mixture
10 is stirred with a thin stainless steel spatula inserted through a small opening in the top of gas inlet adapter. Constant, slow stirring is performed due to the small scale used and the requirement that ingredients be mixed but not spread upward on the tube surface. This assures that all material is available for reaction.

15 Next, 2.2343 grams (1.125 m Mole) of polybutylene adipate (MW=1986, Eq. wt. =993) and 0.6442 g (2.5741 mMole) of MDI is weighed to four decimal places directly into the reaction tube using an analytical balance placed in a glove bag which is flushed and filled with argon. All reactants are carefully placed onto the bottom of the reaction tube. The
20 reactor tube is then removed from the glove bag with the head adapter already in place the mixture is heated while stirring at 100-110°C for one hour during which time it becomes moderately viscous. The reaction tube is lifted just out of the molten metal bath, which is then heated rapidly up to 197-200°C. Then, 0.1177 g (1.3063 mMole) of 1,4-BD is quantitatively carefully
25 added directly onto the still argon flushed prepolymer mixture from a preweighed 1000 microliter syringe, which is also reweighed after addition of 1,4-BD to insure accurate weight addition by difference. Immediately after this 0.0146 g (0.0688 mMole) of Compound 1 is added, also carefully placing it on top of the reaction mixture. The end capper, diethyleneglycol ethyl
30 ether, 0.0107 g (0.0797 mMole) is then added from a microsyringe, again weighing the syringe before and after the addition. These additions are performed while maintaining the argon flow. As soon as the additions are

complete, the reactor tube is lowered back into the Woods metal bath and the mixture is heated at 197-200°C while carefully stirring for 30 minutes.

The total reactive hydroxyl content of the reaction mixture is 5.1476 mMole, while the total isocyanate content is 5.1484 mole. The Compound 1 hydroxyl content represents 5 mMolar % replacement of butanediol mMolar hydroxyl content. Table 4 shows the quantities of all components that will be used to prepare the polymer.

Table 4

Component	Weight (g)	Component Amount (mMole)	Hydroxyl Amount (mMole)	Isocyanate Amount (mMole)
PBA ^a	2.2343	1.125	2.250	0
MDI	0.6442	2.5742	0	5.1484
1,4-BD	0.1177	1.3057	2.6115	0
Compound 1	0.0146	0.0688	0.2064 ^b	0
End Capper ^c	0.0107	0.0797	0.0797	0
Total:	3.0215	N/A	5.1476	5.1484

a - polybutyleneadipate

b - this number of moles includes the three hydroxyl groups of Compound 1

c - diethylene glycol ethyl ether (MW=134.18); dried over Fluka 3A molecular sieves.

While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely descriptive, rather than limiting, and that various changes may be made without departing from the spirit of the scope of the invention

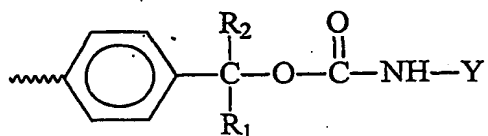
REVERSIBLE CROSSLINKED POLYMERS,
BENZYL CROSSLINKERS AND METHOD

CLAIMS

We claim:

- 1 1. A polymer having a crosslinked structure wherein the crosslinked structure
2 comprises one or more urethane bonds made by the reaction of a benzylic
3 hydroxyl group and an isocyanate group.
1
2
- 1 2. The polymer according to Claim 1, wherein one or more urethane bonds
2 made by the reaction of a benzylic hydroxyl group and an isocyanate group
3 are also present in the polymer backbone of individual polymer chains.
- 1 3. A polymer having a crosslinked structure wherein the crosslinked structure
2 comprises one or more urethane bonds made by the reaction of a benzylic
3 hydroxyl group and an isocyanate group, wherein one or more of said
4 urethane bonds begins to dissociate at a temperature above about 150°C
- 1 4. The polymer according to Claim 3, wherein one or more urethane bonds
2 made by the reaction of a benzylic hydroxyl group and an isocyanate group
3 are also present in the polymer backbone of individual polymer chains,
4 wherein one or more of said urethane bonds begins to dissociate at a
5 temperature above about 150°C..

5. The polymer according to Claim 1, wherein said crosslinked structure comprises



wherein R_1 is H, and R_2 represents a group selected from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen groups; and Y represents a group selected from an isocyanate residue.

6. The polymer according to Claim 5, wherein said isocyanate residue is selected from the group consisting of monoisocyanate, diisocyanate, and triisocyanate residues.

7. The polymer according to Claim 5, wherein said isocyanate residue is selected from the group consisting of aromatic monoisocyanate, aromatic, diisocyanate, aromatic triisocyanate, benzylic monoisocyanate, benzylic diisocyanate, benzylic triisocyanate, aliphatic monoisocyanate, aliphatic diisocyanate, and aliphatic triisocyanate residues.

8. The polymer according to Claim 5, wherein said polymer comprises a polyurethane and 0.01 to 99% of the urethane bonds in said polyurethane are obtained by reaction between a benzylic hydroxyl group and an isocyanate group.

9. The polymer according to Claim 5, wherein said polymer comprises a polyurethane and 0.1 to 50% of the urethane bonds in said polyurethane are obtained by reaction between a benzylic hydroxyl group and an isocyanate group.

10. A polymer having a crosslinked structure comprising:

- a. a polyol with a high molecular weight;
- b. a polyisocyanate;
- c. a polyol with a low molecular weight;
- d. a trifunctional crosslinking compound selected from the group

comprising:

(1) a compound having one benzylic hydroxyl group and two aliphatic hydroxyl groups;

(2) a compound having two benzylic hydroxyl groups and one aliphatic hydroxyl group;

(3) a compound having three benzylic hydroxyl groups;

wherein 0.01 to 99 mol % of bonds in said crosslinked structure comprise urethane bonds obtained by the reaction between a benzylic hydroxyl group and an isocyanate group.

11. A polymer having a crosslinked structure comprising:

- a. a polyol;
- b. a polyisocyanate;
- c. a trifunctional crosslinking compound selected from the group

comprising:

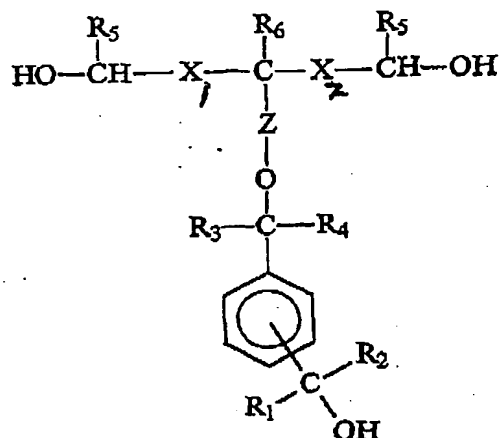
(1) a compound having one benzylic hydroxyl group and two aliphatic hydroxyl groups;

(2) a compound having two benzylic hydroxyl groups and one aliphatic hydroxyl group;

(3) a compound having three benzylic hydroxyl groups;

wherein 0.01 to 99 mol % of bonds in said crosslinked structure comprise urethane bonds obtained by the reaction between a benzylic hydroxyl group and an isocyanate group.

- 1 12. A compound comprising:



- 2 wherein R₁ and R₂ are identical or different and represent a group selected
 3 from -H, hydrocarbon groups containing up to ten carbon atoms, and halogen
 4 groups; wherein R₃ and R₄ are identical or different and represent a group
 5 selected from -H, and hydrocarbon groups containing up to ten carbon atoms;
 6 R₅ represents hydrogen, methyl, ethyl, or propyl; R₆ represents hydrogen,
 7 methyl, or ethyl; X₁ (left arm), X₂ (right arm) and Z may be the same or
 8 different and represent none (no additional segment present), methylene,
 9 ethylene, or *p*-phenylene; the benzylic hydroxyl moiety may be positioned the
 10 para, meta or ortho position.

- 1 13. The compound according to Claim 12 comprising:

2 2-[[[(4-hydroxymethyl)benzyl]oxy]-1,3-propanediol.

- 1 14. The use of the compound according to Claim 12 to crosslink
 2 neighboring polymer chains.

- 1 15. The use of the compound according to Claim 13 to crosslink
 2 neighboring polymer chains.

- 1 16. A compound comprising: a poly-benzylic hydroxyl group capped
 2 polymer or oligomer obtained by reacting compounds containing one primary

3 aliphatic hydroxyl group and one or more benzylic hydroxyl groups with low
4 molecular weight polyisocyanates in a molar ratio of one primary aliphatic
5 hydroxyl group per isocyanate group in the polyisocyanate.

1 17. Crosslinker compositions consisting of bis-isocyanate capped low
2 molecular weight polyols, which structures result from the reaction of 2-20
3 moles of diisocyanates as represented by OCN-R-NCO where R is aliphatic,
4 cycloaliphatic, bisbenzylic, or aromatic, with 1 mole of low molecular weight
5 diols which include aliphatic diols with from 2 to 18 carbon atoms,
6 cycloaliphatic diols with from 5 to 12 carbon atoms and bis-(beta-
7 hydroxyethyl) or bis-(beta-hydroxyethoxy) substituted aromatic rings,
8 including benzene, naphthalene, pyridine or pyrazine rings.

1 18. The use of the crosslinker compositions of Claim 17 to crosslink
2 polymers containing 1 or more pendant benzylic hydroxyl groups on the
3 backbone of the polymer.

1 19. Crosslinker composition consisting of isophorone diisocyanate or TMXPI
2 diisocyanate capped 1,4-butane diol such that a short oligomeric product
3 described by the formula or expression
4

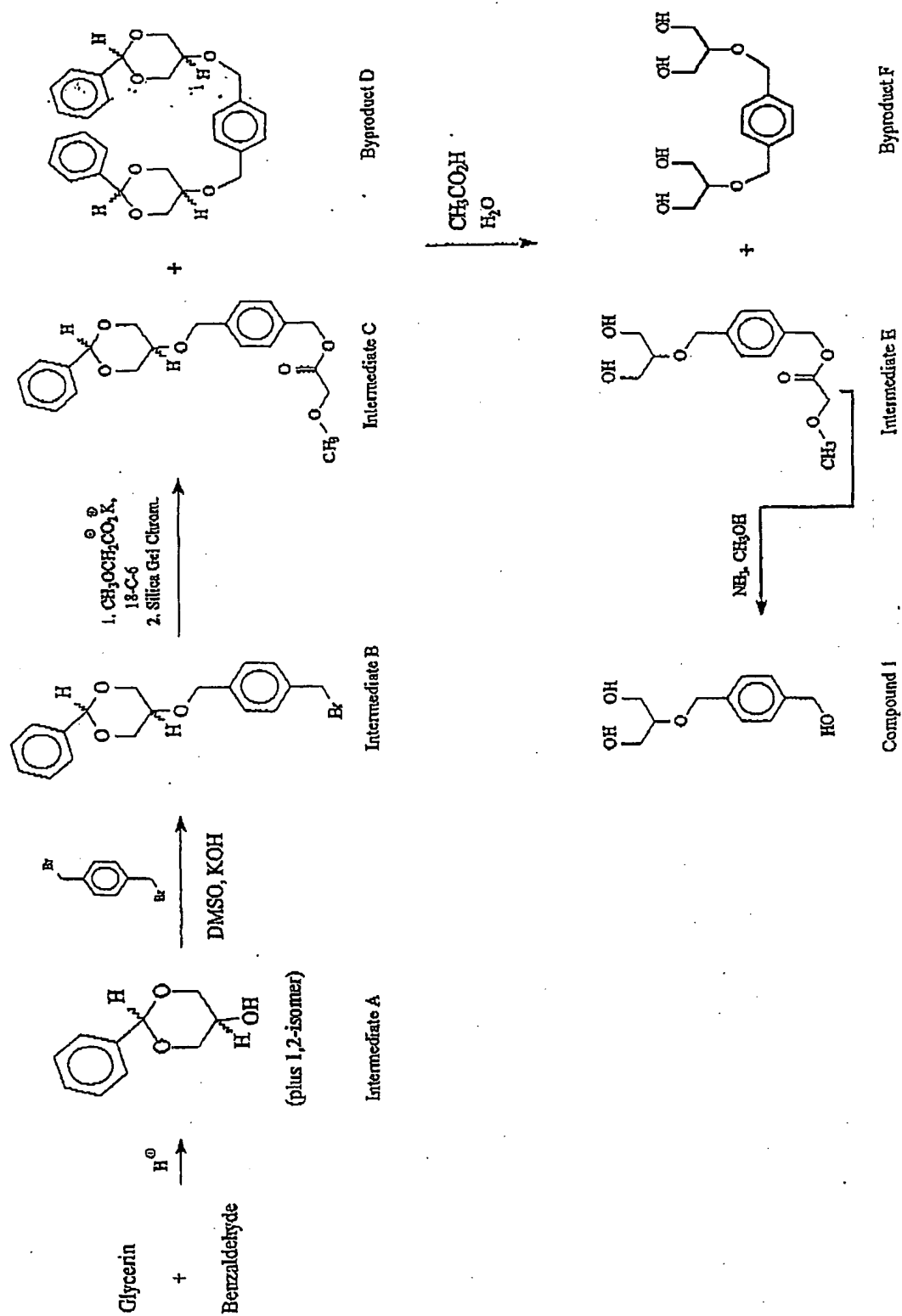


6 where $n = 0, 1, 2, 3, 4, 5$, etc. but is predominately 0.
7

8 is provided, and in which IPDI may be replaced with TMXDI, and is useful as
9 a crosslinker of polymers containing pendant benzylic-hydroxyl groups.

20. Any and all novel features or combination of features, disclosed in the
specification of this application.

SYNTHETIC ROUTE TO PREPARE BLOCKED AND UNBLOCKED TRIFUNCTIONAL CROSSLINKING COMPOUNDS



INTERNATIONAL SEARCH REPORT

Inter Application No
PCT 00/14722

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/80 C08G18/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) & JP 11 322886 A (TOYOCO CO LTD), 26 November 1999 (1999-11-26) abstract	1-15, 20
X	US 4 683 279 A (MILLIGAN BARTON ET AL) 28 July 1987 (1987-07-28) examples 2, 4	17, 20
X	US 4 171 298 A (MINAGAWA MOTONOBU ET AL) 16 October 1979 (1979-10-16) column 35, line 50 - line 61 column 16, line 43 - column 17, line 23 -/-	12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

8 February 2001

Date of mailing of the international search report

15/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Neugebauer, U

INTERNATIONAL SEARCH REPORT

Inte Application No
PC 00/14722

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 188 716 A (SCHWERZEL THOMAS ET AL) 23 February 1993 (1993-02-23) column 1, line 41 -column 4, line 3 column 4, line 62 -column 6, line 10 -----	17-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/14722

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11322886 A	26-11-1999	NONE	
US 4683279 A	28-07-1987	AT 81336 T DE 3782098 A EP 0252425 A JP 63022553 A	15-10-1992 12-11-1992 13-01-1988 30-01-1988
US 4171298 A	16-10-1979	JP 53056239 A US 4298520 A	22-05-1978 03-11-1981
US 5188716 A	23-02-1993	DE 3906143 A AT 88742 T AU 616834 B AU 5019990 A BR 9000884 A CA 2010431 A CN 1045273 A, B DE 59001280 D EP 0385293 A ES 2055187 T JP 2804143 B JP 3007777 A KR 137136 B ZA 9001467 A	06-09-1990 15-05-1993 07-11-1991 06-09-1990 13-02-1991 29-08-1990 12-09-1990 03-06-1993 05-09-1990 16-08-1994 24-09-1998 14-01-1991 25-04-1998 27-11-1991